Rapid Assessment of Soil Metal Concentrations Along the Animas River, New Mexico

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ABSTRACT

Problem: On August 5th, 2015 an inadvertent breech at a mining facility in Colorado spilled 3 million gallons of metal laden wastewater into the Animas River. **Soil Quality Assessment Team**: Texas Tech University (TTU) features the largest non-land grant College of Agriculture in the United States with specialized expertise in proximal soil sensing; New Mexico State University (NMSU) is the land grant university of New Mexico with a field research station in Farmington, a town affected by the spill; US Department of Agriculture – Natural Resources Conservation Service (USDA-NRCS) is the chief agency tasked with providing American farmers and ranchers with financial and technical assistance to voluntarily implement conservation practices, enhance environmental quality, and optimize agricultural operations. **Technology Utilized**: Portable x-ray fluorescence spectrometry, capable of quantifying elemental concentrations in soils with parts per million accuracy on–site in 60 seconds. **Key Findings**: Areas of metal laden sludge showed higher levels of Fe, Cu, Zn, As, and Pb relative to natural soils of the area. The sludge itself exceeds the residential screening limits of permissible metals levels in soils. **Moving Forward**: While the initial large plume of sludge pollution has moved downstream, large areas of the sludge were deposited along riverbanks, fouling such areas to this day. As these materials are slowly eroded and moved downstream, concerns exist over metal accumulation in soils of the Animas River Valley where farmers use Animas River water for irrigation of their crops. **Operational Plans**: While other agencies are chiefly tasked with cleanup, our soil quality assessment team (TTU, NMSU, USDA-NRCS) has a plan in place to work with local farmers and provide long term monitoring of metal levels in irrigated fields from Colorado through the Navajo Nation to ensure soil quality is not degraded by use of Animas River water for crop irrigation. This plan has been submitted to the chief of USDA-NRCS for consideration and funding.

INTRODUCTION

On August 5th, 2015 an inadvertent breech of a mine shaft holding metal laden waters in Colorado was spilled into the Animas River and traversed many areas of southwest Colorado and northwest New Mexico. Farming communities in the area frequently draw irrigation water from the Animas, raising concerns that metal-laden water in the river was and/or will be spread across farm fields as irrigation water. As the plume of pollution moved down the river as a bright orange, cloudy suspension, New Mexico State University was instrumental in collecting numerous soil samples from irrigation ditches and surrounding farm fields in the vicinity of Aztec and Farmington, New Mexico prior to impact by the

pollution plume. These samples will be invaluable in establishing the metal concentrations in the irrigation ditches and farmlands prior to the Gold King Mine spill.

As the pollutant plume moved down the river, a reddish orange sludge was deposited in the river sediment and along the riverbanks. Initially, river water carrying the pollutant plume was cloudy as the sludge was suspended in the water. However, after several weeks, the initial plume ran its course downstream and the water now running down the Colorado portion of the Animas River near Durango appears quite clear; so clear in fact that the coating of the reddish orange sludge on the bottom of the river and adjacent banks is readily apparent (Fig. 1). Luckily, as the initial plume of contamination was moving down the river, residents in Aztec, Farmington, and the Navajo Nation had the opportunity to shut off their irrigation ditches, preventing the most contaminated of the water from entering their fields via irrigation water. The concern now is a much more insidious one, whereby the remaining sludge in the river will slowly be carried downstream as irrigation ditches are once again activated (Fig. 2) and irrigation resumes. In this instance, the water will likely appear quite clear and useable, but the likelihood of small amounts of metals contained in the slowly-migrating sludge will have the potential to accumulate in farm fields over time. Irrigation ditches, operated by a number of cooperatives and private companies, take water from the Animas River and spread it to adjacent farms all up and down the Animas River Valley (Fig. 2). Since northwestern New Mexico receives <10 inches of annual rainfall, agronomic production would not be possible without irrigation water from the river.

In an effort to rapidly respond to the threat to soil health in the farm fields of the area, a collaboration was established between the USDA-Natural Resources Conservation Service (NRCS), New Mexico State University (NMSU), and Texas Tech University (TTU); each has specific strengths that can be utilized in addressing soil quality concerns. The NRCS is widely known and accepted as an agency that partners with farmers to optimize their soil health and agronomic production through the use of improved tillage practices, conservation structures, etc. In fact, many farmers enjoy the benefits of enrolling their land in conservation programs such as the Environmental Quality Incentives Program (EQIP). As such, farmers are fond of working with NRCS and trust their personnel given decades of faithful environmental stewardship. In the same vein, New Mexico State University has a field research station established on land leased from the Navajo Nation nearby to Farmington whereby its faculty can provide direct agronomic research and outreach efforts. Dr. Lombard lives in Aztec, farms several acres, and irrigates his property with water from the Animas River. As such, he can directly understand and sympathize with local farmer concerns as he personally faces the same concerns for his property. In partnering with Texas Tech University, NMSU and the NRCS were able to link up with a research group utilizing state of the art X-ray fluorescence spectrometry for rapid, on-site analysis of soil elemental composition. This technology will be featured in two phases of the project: 1) initial, rapid, on-site assessment of metal levels in soils of the Animas River Valley, and 2) long term monitoring whereby temporal accumulations of metals can be studied and documented as irrigation with river water once again resumes.

MATERIALS AND METHODS

Portable X-ray fluorescence (PXRF) spectrometry is a novel, yet widely accepted means of rapid elemental assessment in soils and sediments. Reference methods for the technique have been developed both by the NRCS (Soil Survey Staff, 2014) and Environmental Protection Agency (US-EPA, 2007)(Method 6200) for use in soils and sediments. Essentially, the PXRF spectrometer is a handheld unit that uses low power X-rays to eject inner shell electrons from various elements. As this occurs, outer shell electrons then

cascade down to fill inner shell voids, but in doing so much relinquish energy, termed *fluorescence*. The fluorescence energy is precisely measured via an integrated silicon drift detector and used to both identify which elements are present as well as their abundance. The operational theory, optimized uses, limitations and applications are summarized by Weindorf et al. (2014). Traditional elemental soil analysis relies upon digestion with caustic acids (US-EPA 1996a, 1996b), filtration, and elemental quantification via inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Soltanpour et al., 1996). Whilst the ICP-AES technique is highly accurate and will remain the analytical standard for the foreseeable future, it is laboratory-based equipment and requires extensive sample processing, consumables, etc. With regards to analytical accuracy, the PXRF reported elemental values are typically within 5-10% of the certified elemental concentrations (determined via ICP-AES), only the PXRF reported values can be obtained on-site in 60 sec. Both techniques allow for multi-elemental analysis; quite commonly ~20 elements are reported by each instrument.

For rapid analysis of elemental concentrations on-site, the NRCS-NMSU-TTU team used a Delta Premium (DP-6000) PXRF featuring a Rh X-ray tube operated at 10-40 keV with elemental quantification accomplished via integrated ultra-high resolution (<165 eV) silicon drift detector. Scanning was conducted in a proprietary software configuration known as Geochem Mode which offers elemental quantification of the following elements: V, Cr, Fe, Co, Ni, Cu, Zn, W, Hg, As, Se, Pb, Bi, Rb, U, Sr, Y, Zr, Th, Mo, Ag, Cd, Sn, Sb, Ti, Mn, Mg, Al, Si, P, S, Cl, K, and Ca. Geochem mode consists of two beams; each was set to scan for 30 sec, such that one complete sample scan took 60 sec. General limits of detection for each element are provided as Fig. 3. However, the data generated by the PXRF whilst scanning provides both the elemental quantity on an element by element basis, as well as the error term for each measurement (e.g., Pb 250 mg kg^{-1}; ±5 mg kg^{-1}). Furthermore, the location of each soil scanned was georeferenced with a handheld GPS unit to catalog the location of metals/elements detected. PXRF performance was assessed via scanning of two NIST certified soil standards whereby PXRF elemental quantity was compared to certified reference values with a recovery percentage calculated on an element by element basis.

RESULTS AND DISCUSSION

On-site PXRF scanning was undertaken Sept. 1-3, 2015. In doing so, multiple types of land were evaluated to include: irrigated lands (water taken from the Animas River), non-irrigated lands (Control), and riverbank sediment. Notably, the riverbank sediment was observed to be a mix of natural alluvial sediment and Gold King Mine sludge; the two of which had substantively different elemental signatures. In total, 140 samples were scanned in three days. Summary results are provided in Table 1.

Table 1. Elemental concentration ranges and averages for soils and sediments scanned with PXRF in the Animas River Valley in Colorado and New Mexico. All units are in mg kg^{-1}.

n	Location	Al Avg	Al Range	Fe Avg	Fe Range	Cu Avg	Cu Range	Zn Avg	Zn Range	As Avg	As Range	Pb Avg	Pb Range
29	Control	64087	25413-83540	28987	9047-50892	33	ND-94	117	25-330	7	ND-13	53	12-230
67	Irrigated	53541	7281-80325	28514	4430-48232	36	11-100	175	39-819	7	ND-13	67	5-271
35	Riverbank	37749	4218-80108	38302	5818-293194	77	ND-220	365	19-1068	11	ND-38	153	10-487
9	Riverbank-Sludge	21018	8730-38781	48355	38292-75959	137	90-176	474	277-1174	40	ND-54	637	509-859
140													

Notably, we found and identified the properties of the river sludge sent down the Animas River. Generally, it has Pb levels of ~600-800 mg kg^{-1}; and higher levels of Fe, Cu, and Zn. The residential screening limit for Pb in soils is 400 mg kg^{-1} (Brevik, 2013). These sludge materials were found both in New Mexico and Colorado, both on the stream banks and underwater (Fig. 4). Irrigated lands along the Animas River tended

to have slightly higher levels of metals than non-irrigated "control" areas. It is essential we monitor these areas over time as more sludge sediment washes down the river and can potentially be spread out via irrigation. PXRF was highly effective at quickly collecting elemental data with results verified both by NIST certified standards and ICP analysis. The variance of PXRF data relative to certified values is ~5-10%. Extensive river pollution was found from the Colorado/New Mexico border headed north; this sludge is highly likely to move down into New Mexico over time in response to hydrologic pulses (snow melt, flash floods, etc.).

Summarily, the level of metals found in sludge along the Animas River warrants careful observation. Certainly, cleanup of the sludge is recommended in areas where it is apparent and accessible. Nonetheless, it is highly likely that small amounts of metal will continue to work their way downstream intermixed in alluvial sediments for the next several years (Fig. 5). This poses a risk of accumulation in soils whereby Animas River water is used for irrigation. Extensive spatial and temporal sampling are recommended such that the levels of metals in soils of the Animas River Valley will be more thoroughly understood in an effort to protect and optimize soil health. If areas of accumulation are noted, phytoremediation or other remediation strategies should be undertaken to ensure that the metal laden soils do not pose a risk for metal bioaccumulation in plants or feedstocks used by humans or animals.

The NRCS, NMSU, and TTU have already submitted an extensive multi-year monitoring plan for funding consideration by the national NRCS. We stand ready to assist farmers and land owners in the region in protecting the food and fiber generated on lands of historically high agronomic value.

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Fig. 1. Clear Animas River water north of Durango, Colorado showing remnants of the reddish orange colored sludge both along the river banks as well as submerged underwater.

Fig. 2. Irrigation ditches and pumps of the Animas River Valley used for spreading river water to farm fields.

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Limits of Detection

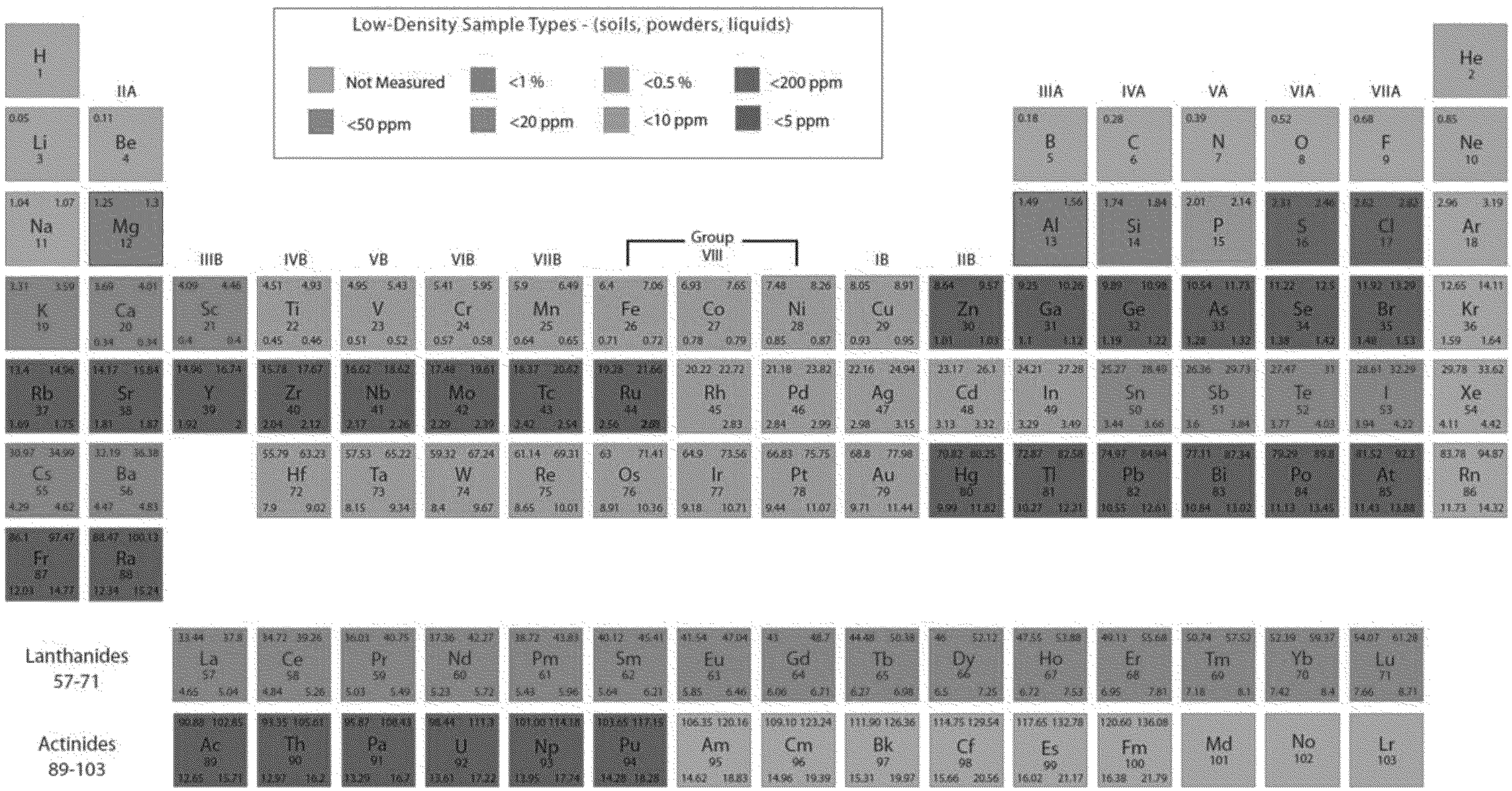

Fig. 3. Generalized limits of detection for the Delta PXRF by Olympus.

Fig. 4. Assessment of sludge laden sediment with portable x-ray fluorescence spectrometry along the banks of the Animas River in New Mexico.

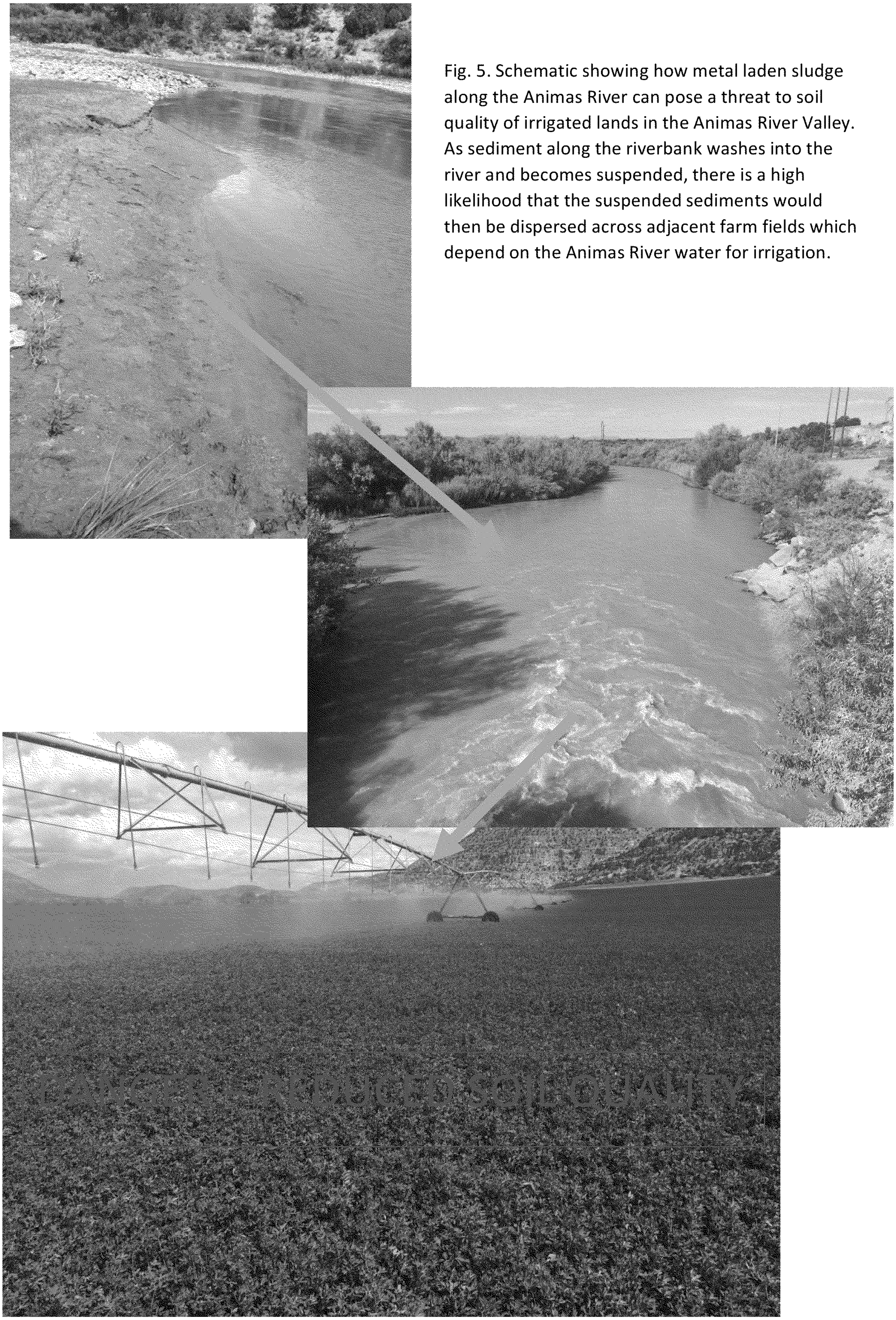

Fig. 5. Schematic showing how metal laden sludge along the Animas River can pose a threat to soil quality of irrigated lands in the Animas River Valley. As sediment along the riverbank washes into the river and becomes suspended, there is a high likelihood that the suspended sediments would then be dispersed across adjacent farm fields which depend on the Animas River water for irrigation.